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(54) **LASER NITRIDING METHOD OF MAKING PHOSPHOR BRONZE WITH SURFACE-EMBEDDED TITANIUM CARBIDE PARTICLES**

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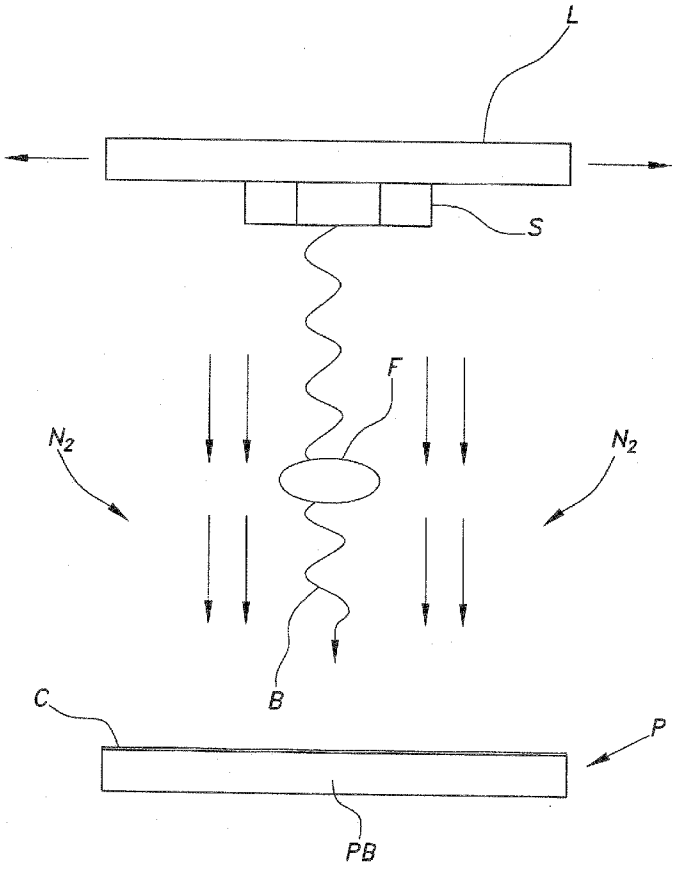
USPC **427/554**

(57) **ABSTRACT**

The laser nitriding method of making phosphor bronze with surface-embedded titanium carbide particles involves coating a cleaned phosphor bronze workpiece with a thin film formed of a carbonaceous layer mixed with nanosize particles of titanium carbide. The titanium carbide forms about 5 wt % of the thin film, and the phosphor bronze workpiece is composed of about 6.0 wt % tin, about 0.1 wt % phosphorous, and about 93.9 wt % copper. A laser beam is then scanned over the thin film formed on the phosphor bronze workpiece. Coaxially and simultaneously with the laser beam, a stream of nitrogen gas is sprayed on the thin film formed on the phosphor bronze workpiece in order to provide the workpiece with a nitride coating having nanoparticles of titanium carbide embedded therein.



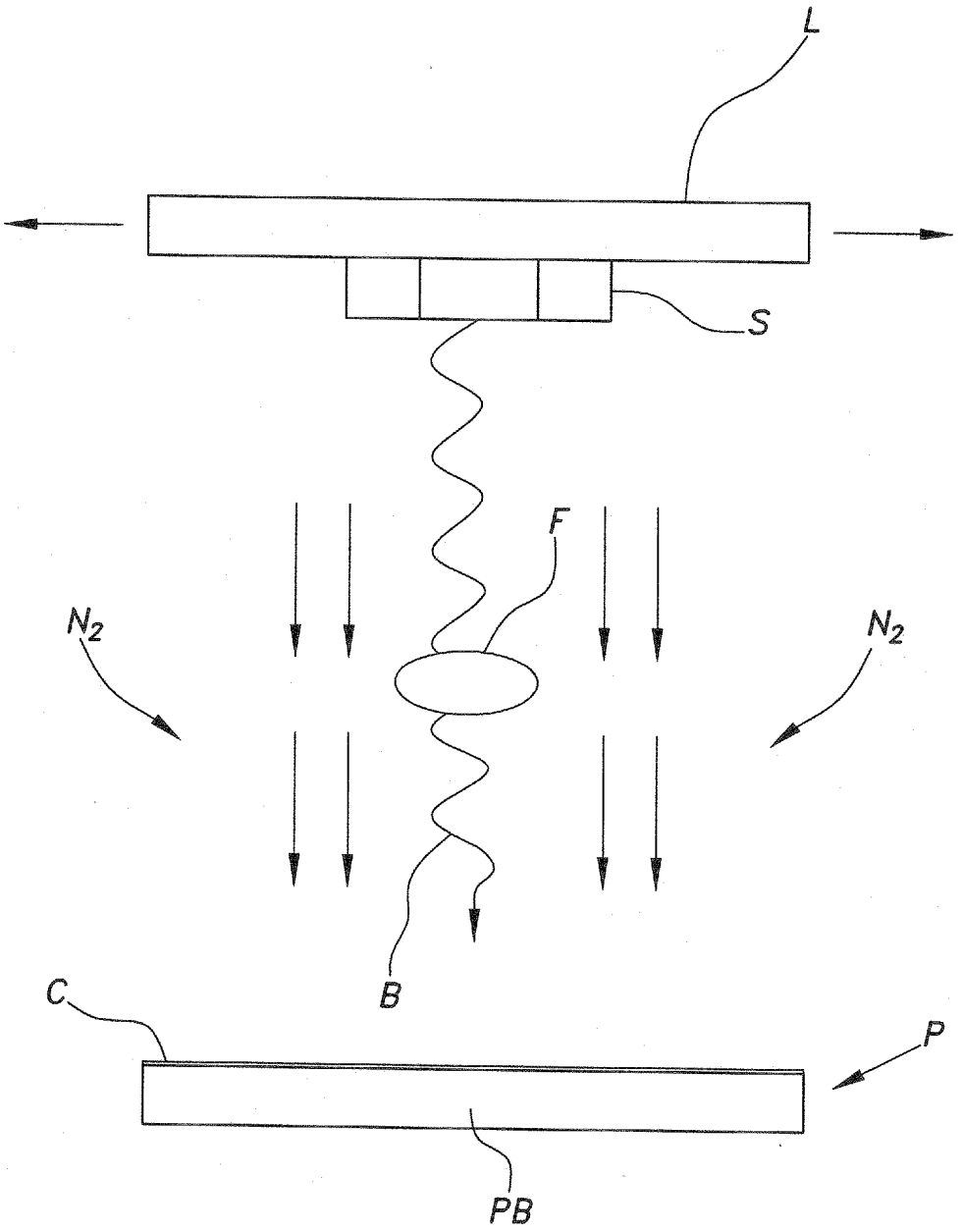


Fig. 1

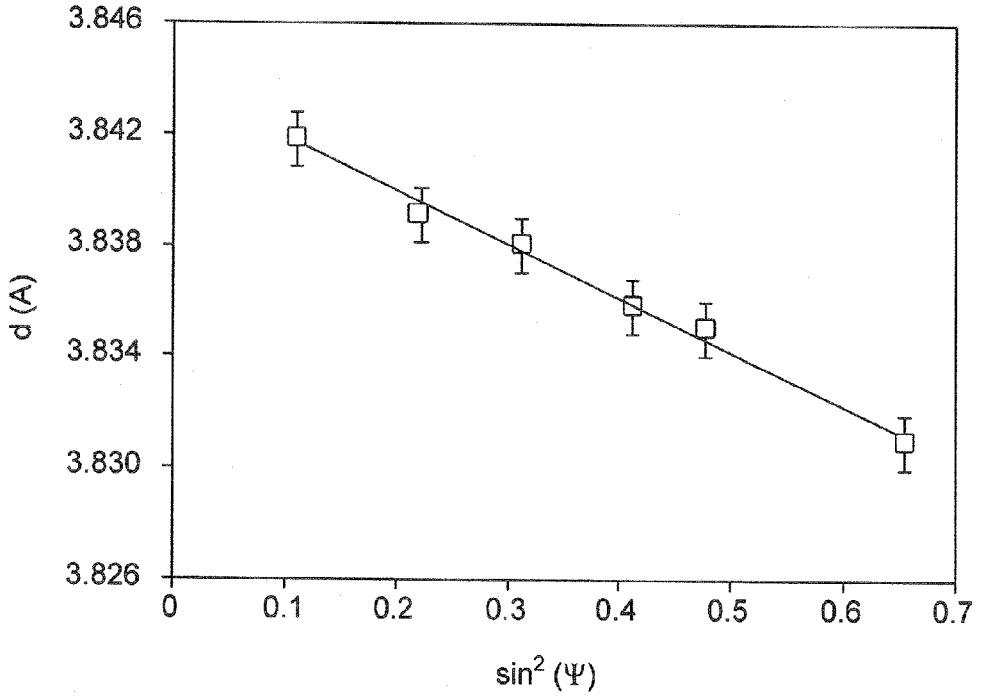


Fig. 2

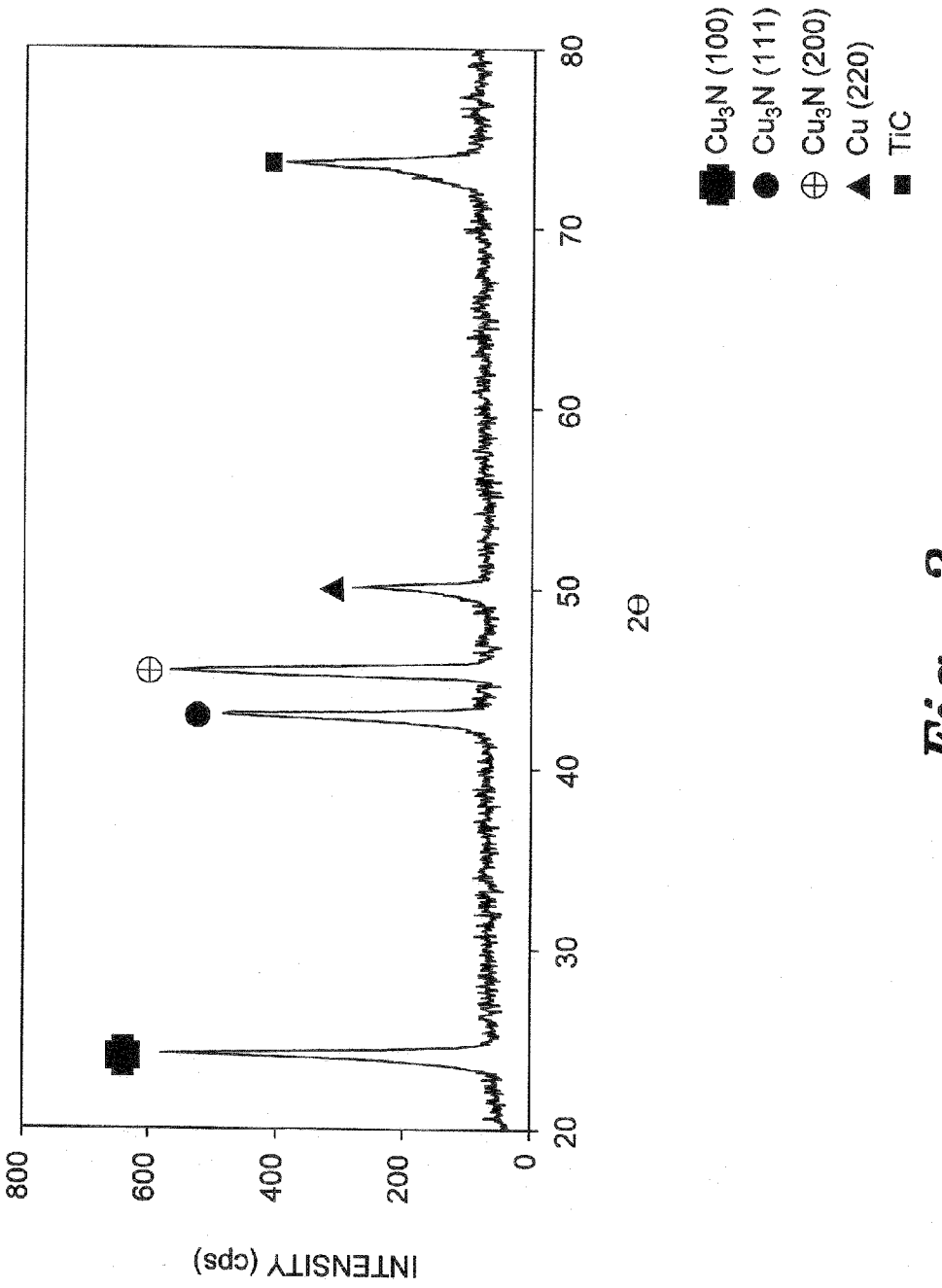

INTENSITY (cps)
800
600
400
200
0
20
30
40
50
60
70
80
2Θ
Cu3N (100)
Cu3N (111)
Cu3N (200)
Cu (220)
TiC

Fig. 3

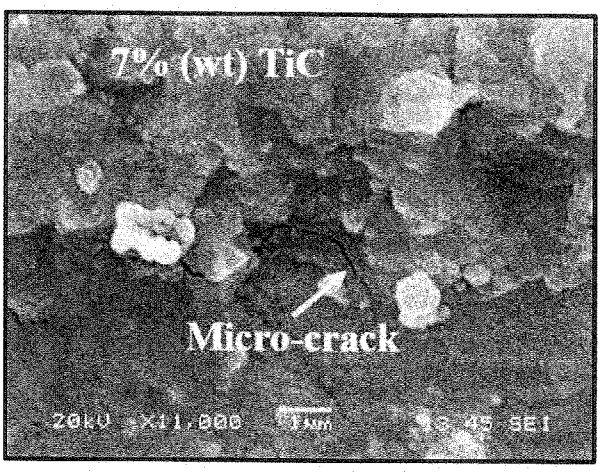

7% (wt) TiC
Micro-crack
20kV X11,000 1μm 13 45 SEI

Fig. 4A

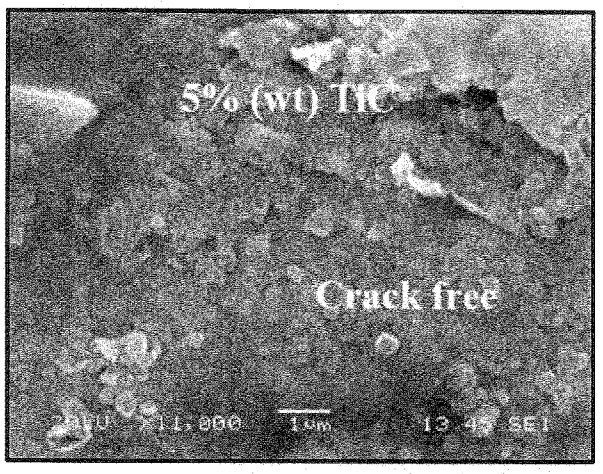

5% (wt) TiC
Crack free
20kV X11,000 1μm 13 45 SEI

Fig. 4B

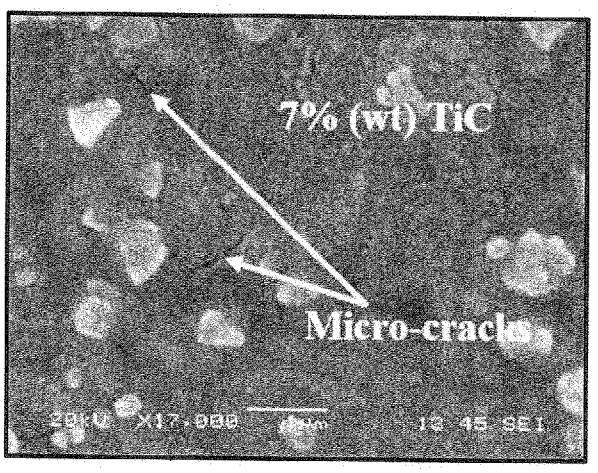


Fig. 5A

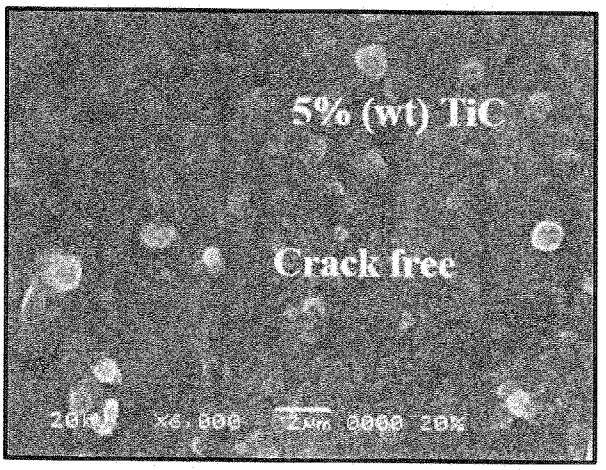


Fig. 5B

LASER NITRIDING METHOD OF MAKING PHOSPHOR BRONZE WITH SURFACE-EMBEDDED TITANIUM CARBIDE PARTICLES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of U.S. patent application Ser. No. 13/712,859, filed Dec. 12, 2012.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to processes for hardening metal surfaces, and particularly to a laser nitriding method of making phosphor bronze with surface-embedded titanium carbide particles.

[0004] 2. Description of the Related Art

[0005] Phosphor bronze (sometimes sold with the shorter name Phos Bronze) is an alloy of copper with 3.5 to 10% of tin and a significant phosphorus content of up to 1%. The phosphorus is added as deoxidizing agent during melting. These alloys are notable for their toughness, strength, low coefficient of friction, and fine grain. The phosphorus improves the fluidity of the molten metal, thereby improving castability, and also improves mechanical properties by cleaning up the grain boundaries. Phosphor bronze is used for springs, bolts and various other items used in situations where resistance to fatigue, wear and chemical corrosion are required (e.g., a ship's propellers in a marine environment). The alloy is also used in some dental bridges.

[0006] Improvement of tribological properties of the alloy surface would facilitate the use of the enhanced alloy in harsh environments. It would be particularly desirable to be able to enhance the surface of a phosphor bronze workpiece with titanium carbide, which is known to provide a wide variety of surface-enhancing properties to alloys. Embedding the necessarily very small particles of titanium carbide in just the surface layer, however, is extremely difficult, and cannot be accomplished by conventional metallurgical methods.

[0007] Thus, a laser nitriding method of making phosphor bronze with surface-embedded titanium carbide particles solving the aforementioned problems is desired.

SUMMARY OF THE INVENTION

[0008] The laser nitriding method of making phosphor bronze with surface-embedded titanium carbide particles provides a method of hardening the surface of phosphor bronze workpieces. A cleaned phosphor bronze workpiece is first coated with a thin film formed of a carbonaceous layer mixed with powdered titanium carbide. The powdered titanium carbide forms about 5 wt % of the thin film, and the phosphor bronze workpiece is composed of about 6.0 wt % tin, about 0.1 wt % phosphorous, and about 93.9 wt % copper. A laser beam is then scanned over the thin film formed on the phosphor bronze workpiece. Coaxially and simultaneously with the laser beam, a stream of nitrogen gas is sprayed onto the thin film formed on the phosphor bronze workpiece in order to embed particles of the titanium carbide into a surface layer of the phosphor bronze workpiece.

[0009] These and other features of the present invention will become readily apparent upon further review of the following specification and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] FIG. **1** is a diagram illustrating the laser nitriding method of making phosphor bronze with surface-embedded titanium carbide particles according to the present invention.

[0011] FIG. **2** is a graph illustrating the d-spacing measurement as a function of $\sin^2 \psi$ for X-ray diffraction (XRD) analysis of a sample of phosphor bronze treated by the laser nitriding method of making phosphor bronze with surface-embedded titanium carbide particles according to the present invention.

[0012] FIG. **3** is a XRD diffractogram comparing diffraction intensities of an untreated phosphor bronze workpiece with a sample of phosphor bronze treated by the laser nitriding method of making phosphor bronze with surface-embedded titanium carbide particles according to the present invention.

[0013] FIG. **4**A is a scanning electron micrograph showing a cross section in the surface region of the laser-treated layer of a sample of phosphor bronze treated by laser nitriding phosphor bronze with surface-embedded titanium carbide particles at a titanium carbide concentration of 7 wt %, illustrating cracks extending into the treated layer.

[0014] FIG. **4**B is a scanning electron micrograph showing a cross section in the surface region of the laser-treated layer of a sample of phosphor bronze treated by laser nitriding phosphor bronze with surface-embedded titanium carbide particles at a titanium carbide concentration of 5 wt %, showing a crack-free treated layer, as compared to FIG. **4**A.

[0015] FIG. **5**A is a scanning electron micrograph showing a top view of the laser-treated surface layer of the sample of phosphor bronze of FIG. **4**A, showing cracks extending across portions of the top surface of the laser-treated layer at a 7 wt % TiC concentration.

[0016] FIG. **5**B is a scanning electron micrograph showing a top view of the laser-treated surface layer of the sample of phosphor bronze of FIG. **4**B, showing that the laser-treated surface is substantially crack-free at a 5 wt % TiC concentration, as compared to the 7 wt % TiC concentration of FIG. **5**A.

[0017] Similar reference characters denote corresponding features consistently throughout the attached drawings.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] As diagrammatically illustrated in FIG. **1**, following cleaning of a phosphor bronze plate P, a laser beam B is scanned over a surface of the phosphor bronze plate P. Preferably, the laser beam B is produced by a carbon dioxide laser L with a maximum output power of 2 kW. It should be understood that any suitable type of laser may be utilized. Scanning preferably occurs at a rate of about 10 cm/sec. The laser L may be scanned and applied to the surface of the plate P by any suitable method of laser treatment. Such nitriding lasers and laser scanning systems are well known in the art. One such example is shown in U.S. Pat. No. 5,411,770, which is hereby incorporated by reference in its entirety. The laser beam B is focused onto the surface of plate P by a focusing lens F, which may be any suitable type of focusing lens. The optimal focal length of focusing lens F is found to be about 127 mm for a laser beam B having an initial diameter of about 0.9 mm.

[0019] A stream of nitrogen gas, which may be atomic nitrogen dissociated from ammonia at high temperature, is sprayed on the surface of the phosphor bronze plate P coaxi-

ally and simultaneously with the laser beam at a relatively high pressure, thus forming a barrier nitride layer in the laser-irradiated region.

[0020] It should be understood that the sprayer S in FIG. **1** is shown for illustrative purposes only, as is the stream of nitrogen N coaxially surrounding laser beam B. Such nitrogen application for the nitriding of surfaces is well known in the art, and any suitable method for spraying or otherwise applying the nitrogen gas coaxially and simultaneously with laser beam B may be utilized. One such application of nitrogen gas to an alloy surface during nitriding is described in U.S. Pat. No. 4,588,450, which is hereby incorporated by reference in its entirety.

[0021] In the following experiment, the laser surface treatment process was carried out with different laser parameters. It was found that increasing laser output power beyond 90 W resulted in high surface roughness due to melt flow during over-melting of the surface, and also resulted in surface cracks due to high temperature gradients, as well as nitride species formed in the surface vicinity. Alternatively, reducing the laser power below 90 W lowered the depth of the laser treated layer. Additionally, reducing laser scanning speed below 10 cm/s increased the surface roughness due to over-melting of the surface, while increasing the speed reduced the laser treatment depth. Thus, laser parameters resulting in crack-free surfaces with low surface roughness were selected.

[0022] The optimal laser treatment conditions are given below in Table 1. As shown in Table 1, nitrogen gas (N_2) was injected via a coaxial nozzle at a pressure of 600 kPa, a nozzle diameter of 1.5 mm, and a nozzle gap size of 1.5 mm. The laser treatment experiments were repeated three times to ensure the same topology at the surface and similar microstructures in the treated layer. In Table 1, it should be noted that the frequency is the laser pulse frequency, as opposed to the frequency of the light emitted.

TABLE 1

Optimal Laser Treatment Parameters

Scanning Speed (cm/s) (mm/min)	Power (W)	Frequency (Hz)	Nozzle Gap (mm)	Nozzle Diameter (mm)	Focus setting (mm)	N_2 Pressure (kPa)
10	90	1000	1.5	1.5	127	600

[0023] The plate P is formed from a phosphor bronze workpiece PB having a thin carbonaceous film C formed thereon. The phosphor bronze of workpiece PB has an elemental composition of 6.0 wt % Sn, 0.1 wt % P, and 93.9 wt % Cu. The overall plate P had a thickness of 3 mm, a length of 20 mm, and a width of 10 mm. Rectangular plate samples were used in the experiments.

[0024] In order to form the thin film carbonaceous layer C, a water-soluble phenolic resin was homogenously mixed with 5 wt % of TiC powder having a mean particle size of 400 nm prior to application to the surface of the bronze plate P. The uniform film of the phenolic resin containing 5 wt % TiC powder and having a thickness of 50 μm was formed on the surface of the plate P in a control chamber held at a pressure of 8 bars and a constant temperature of 175° C. for two hours. The plate P was then heated to 400° C. in an argon atmosphere for several hours to ensure the conversion of the phenolic resin into carbon. The carbon layer C containing 5 wt % TiC coated the surfaces of each phosphor bronze workpiece PB, which were then scanned by the laser beam B in the presence of the high pressure nitrogen assist gas according to the parameters given above in Table 1.

[0025] Material characterization of the laser-nitrided surfaces was carried out using scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. A typical setting for the XRD was 40 kV and 30 mA, and the scanning angle (**2θ**) ranged over 20°-80°. Further, a digital microhardness tester was used to determine microhardness at the surface of the nitride layer. The standard test method for Vickers indentation hardness of advanced ceramics (ASTM C1327-99) was used. Microhardness was measured at the plate surface after the laser treatment process. The measurements were repeated five times at each location for consistency of the results.

[0026] Residual stress measurement relies on the stresses in the fine-grained polycrystalline structure. The position of the diffraction peak undergoes a shift as the specimen is tilted by an angle ψ. The magnitude of the shift is related to the magnitude of the residual stress. The relationship between the peak shift and the residual stress σ is given by

$$\sigma = \frac{E}{(1+\nu)\sin^2\psi} \cdot \frac{d_n - d_0}{d_0},$$

where E is the Young's modulus, ν is Poisson's ratio, ψ is the tilt angle, and the d_n are the d-spacings of the diffraction peak measured at each tilt angle, with d_0 representing the spacing at the initial angle.

[0027] If there are no shear strains present in the specimen, the d-spacing changes linearly with $\sin^2\psi$. The d-spacing measurement as a function of $\sin^2\psi$ is shown in FIG. **2**. The calculations were performed for Cu_3N d(100) planes (2θ=23.44)° with an inter-planar spacing of 0.3844 nm. It was observed that no shear strain developed in the specimen surface region, and the residual stress was compressive. The linear dependence of d(100) in FIG. **2** resulted in a slope of $-2.0\times10^{-3}\pm9.12\times10^{-5}$ nm and an intercept of $0.3844\pm4.75\times10^{-3}$ nm. The elastic modulus and Poisson's ratio of phosphor bronze are 96.5 GPa and 0.34, respectively. The residual stress measured was on the order of −380 MPa, and the estimated error is ±10 MPa, or 2.6%. It should be noted that the error is estimated based on three repeats of the XRD measurements.

[0028] SEM of the laser-treated surface showed regular laser scanning tracks with no overflow of molten material observed between the laser scan tracks. The surface cavities and asperities due to surface evaporation were not visible, which indicates that the surface temperature remained below the evaporation temperature of the workpiece during the laser treatment process. Although local heating along the laser scan tracks results in high temperature gradients in this region, thermally induced cracks were not observed at the surface. The color of the workpiece surface was mahogany after the laser treatment process. This indicates that Cu_3N was formed at the surface region after laser treatment. However, randomly scattered, relatively small red regions were also observed at the surface, which indicates the dissolution of Cu_3N at high temperatures. It should be noted that laser-treated surfaces solidify rapidly. Thus, the dissolution of Cu_3N does not extend to a large area at the surface.

[0029] Fine grains were visible at the laser-treated surface. Additionally, some scattered, partially embedded TiC par-

ticles were observed in the SEM micrographs. Since the thermal expansion coefficient of TiC and the base material are different, thermally induced stresses were formed around the TiC particles. However, no microcracks were observed from the SEM micrographs in this region. This may be attributed to the partial dissolution of TiC particles, which modifies the thermal expansion coefficient of the substrate material in this region. Further, laser scanning of multi-tracks at the surface results in an annealing effect on the initially scanned regions. This contributes to stress relaxation at the surface, while minimizing crack formation. The roughness of the laser-treated surface is on the order of 3.2 μm, which is slightly rougher than that of the original workpiece surface of 2 μm. Close examination of the SEM micrographs revealed that the overlapping ratio of the laser spots was on the order of 70%, which, in turn, results in uniform melting of the surface along the scan tracks.

[0030] Examination of SEM micrographs of the cross-section of the laser-treated layer showed that laser scanning of the workpiece at constant velocity resulted in a uniform thickness of the laser-treated layer. The thickness of the laser-treated layer extended to about 50 μm below the surface. It was evident from the SEM micrographs that the cross section of the laser-treated layer consisted of four regions. A dense layer consisting of fine grains was formed in the first region. In this region, the presence of partially melted TiC particles was evident from the SEM micrographs. Formation of Cu_3N in the surface region lowered the density and volume shrinkage in the first layer, which resulted in the development of micro-voids in the dense layer. However, the extent of micro-voids was small and randomly scattered in the dense layer. The high quench rates in the cooling cycle after laser treatment were responsible for the formation of fine grains in the dense region. Although the rate of thermal expansion and contraction of TiC particles and the substrate material are different, no cracks were observed around the TiC particles. This indicates that the residual stress developed in this layer is sufficiently low that it does not trigger crack initiation in the dense layer.

[0031] In the second region, a dendritic structure with elongated grains was observed. The formation of a dendritic structure was due to the high cooling rates, resulting in a high rate of solidification in this region. The non-uniform cooling rates in the surface region of the laser-treated layer were responsible for the development of the elongated grains. In addition, the SEM micrographs showed partially dissolved TiC particles in this region. The presence of fine size voids in this region also indicated volume shrinkage due to nitride species in this region. High cooling rates and volume shrinkage result in the formation of a high level of compressive stress in this region. It should be noted that the surface of the workpiece expands freely during the laser treatment process so that thermally induced stresses in this region are expected to be low. However, the region below the surface vicinity is not free to expand, and compressive stresses are developed in this region. Thus, higher cooling rates and volume shrinkage result in the formation of fine cracks in this region. The cracks act as stress relaxation centers in the surface region. Intergranular cracking is reduced due to the packed dendrite grains, which indicates small micro-stress levels in this region.

[0032] In the third region, small grains with a cellular structure were observed. The cooling rate was relatively slower than that of the surface region. Thus, convective cooling at the surface was replaced with conductive heat transfer. Since the cooling rate was slower, the thermal stress formed was not as great as that of the surface layer. Therefore, no cracks were observed in this region.

[0033] The fourth region was the base material interface region. Although grains were large in this region, there was a clear demarcation line between the heat-affected layer and the base material. The gross dimensions of the heat affected zone (HAZ) were also clearly observed. The position of the HAZ was controlled by the high thermal conductivity of copper, which controls the demarcation line in this region.

[0034] FIG. **3** shows an XRD diffractogram of a plain phosphor bronze plate and a laser-treated workpiece. The presence of Cu_3N [100], Cu_3N [111], Cu_3N [200], and TiC peaks are evident in FIG. **3**. Further, the presence of Cu peaks reveals the dissolution of Cu_3N at the surface during the cooling cycle after the laser treatment process. Table 2 below gives the energy dispersive X-ray spectroscopy (EDS) data for the laser-treated surface. The depth of emission of X-rays due to incident electrons was estimated at about 1 μm.

TABLE 2

EDS Data and Corresponding Locations at the Laser-Treated Surface (wt %)

Spectrum	N	Ti	Sn	Cu
Spectrum 1	5	5	6	84
Spectrum 2	4	5	6	85
Spectrum 3	5	5	7	83
Spectrum 4	3	5	6	86
Spectrum 5	4	5	6	85

[0035] The quantification of light elements, such as nitrogen, in EDS data is very hard to detect. However, the presence of nitrogen was evident at the surface. Detection of no Sn data at the laser-treated surface reveals that some fraction of Sn is evaporated from the surface during the laser treatment process. In addition, the presence of 5 wt % Ti in the EDS data is due to the TiC particles at the surface region of the laser-treated layer.

[0036] In the untreated phosphor bronze sample, microhardness was found to be 140, compared with a measured 320 for the laser-treated plate. The microhardness of the laser-treated surface increased almost three times over that of the plain workpiece surface. The increase in the surface hardness is due to the formation of dense structures at the surface due to high cooling rates and nitride species formation, and also due to the presence of TiC particles at the surface. The residual stress measured by the XRD technique was on the order of 360 MPa. Since the cooling rate is high, self-annealing during the cooling period effectively does not take place, and therefore the residual stress remains high in the surface region. It should be noted that the residual stress measured is limited to the surface vicinity, since the penetration depth of the X-ray radiation is on the order of few μm.

[0037] As noted above, the carbon layer containing 5 t % TiC is selected for optimal results. Even a small adjustment of this concentration can result in the generation of unwanted micro-cracks in the treated material. FIG. **4**A is a scanning electron micrograph showing a cross section of the treated layer in the surface region of a sample of phosphor bronze treated by laser nitriding phosphor bronze with surface-embedded titanium carbide particles at a titanium carbide concentration of 7 wt %. As shown, at a concentration of 7 wt %,

micro-cracks appear in the treated layer near the surface region. By comparison, FIG. **4**B is a scanning electron micrograph showing a cross section of the treated layer in the surface region of a sample of phosphor bronze treated by laser nitriding phosphor bronze with surface-embedded titanium carbide particles, but with the desired optimal titanium carbide concentration of 5 wt %. This sample shows a crack free treated layer. Similarly, FIG. **5**A is a scanning electron micrograph showing a top view of the surface layer of the treated sample of phosphor bronze of FIG. **4**A at a titanium carbide concentration of 7 wt %, clearly showing micro-cracks in the top surface of the laser-treated layer. As shown in FIG. **5**B, the top surface of the laser-treated layer remains crack free when a concentration of 5 wt % is used. Even a small change of concentration of 2 wt % from the optimal 5 wt % can result in the generation of unwanted micro-cracks in the treated material. Thus, a 5 wt % concentration of TiC is preferred.

[0038] The micrograph images of FIGS. **4**A-**5**B were taken from the surface region because high micro-stress levels are most apparent in this region, due to the high cooling rates in the surface region. The mismatch of the thermal expansion coefficients of TiC particles and the base material (i.e., phosphor bronze) results in the development of the micro-stress levels because of the different rates of contraction during the cooling period. As can be clearly seen in the micrograph images, once the particle concentration increases from 5 wt % TiC to 7 wt % TiC, the stress levels exceed the yielding limit of the phosphor bronze, which, in turn, causes crack initiation and formation in the surface region of the laser-treated layer.

[0039] It is to be understood that the present invention is not limited to the embodiments described above, but encompasses any and all embodiments within the scope of the following claims.

We claim:

1. A method of making phosphor bronze with surface-embedded titanium carbide particles, comprising the steps of:

coating a phosphor bronze workpiece with a layer of water-soluble phenolic resin homogeneously mixed with particles of titanium carbide;

heating the water-soluble phenolic resin homogeneously mixed with the particles of titanium carbide to produce a thin film of carbonaceous material having nanometer-sized particles of titanium carbide formed on the phosphor bronze workpiece;

scanning a laser beam over a surface of the phosphor bronze workpiece having the thin film of carbonaceous material containing nanometer-size particles of titanium carbide formed thereon; and

spraying a stream of nitrogen gas on the thin film formed on the phosphor bronze workpiece coaxially and simultaneously with the laser beam to provide the workpiece with a nitride coating having particles of titanium carbide embedded therein, wherein the titanium carbide comprises 5 wt % of the coating.

2. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **1**, wherein the particles of titanium carbide have a mean particle size of about 400 nm.

3. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **1**, wherein the coating step is performed under a pressure of about 8 bars at a constant temperature of about 175° C. for a period of about two hours.

4. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **1**, wherein the layer has a thickness of about 50 μm.

5. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **1**, wherein the step of heating the water-soluble phenolic resin homogeneously mixed with the powdered titanium carbide is performed in an argon atmosphere at a temperature of about 400° C.

6. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **1**, where said scanning step is performed using a carbon dioxide laser.

7. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **6**, wherein said scanning step comprises generating the laser beam with a power output of about 90 W.

8. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **1**, wherein said spraying step comprises spraying nitrogen gas having a pressure of about 600 kPa.

9. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **1**, wherein the step of scanning the laser beam over the thin film comprises scanning the laser beam at a rate of about 10 cm/s.

10. A method of making phosphor bronze with surface-embedded titanium carbide particles, comprising the steps of:

scanning a laser beam over a surface of a phosphor bronze workpiece having a thin film of carbonaceous material containing nanometer-size particles of titanium carbide formed thereon, the phosphor bronze workpiece containing about 6.0% tin, about 0.1 wt % phosphorous, and about 93.9 wt % copper, the thin film of carbonaceous material containing about 5 wt % titanium carbide particles; and

spraying a stream of nitrogen gas on the thin film formed on the phosphor bronze workpiece coaxially and simultaneously with the laser beam to provide the workpiece with a to nitride coating having particles of titanium carbide embedded therein.

11. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **10**, wherein the particles of titanium carbide have a mean particle size of about 400 nm.

12. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **11**, wherein the thin film has a thickness of about 50 μm.

13. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **10**, wherein the scanning step further comprises generating the laser beam with a carbon dioxide laser.

14. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **13**, wherein said step of generating the laser beam with the carbon dioxide laser comprises generating the laser beam with a power output of about 90 W.

15. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **10**, wherein the step of spraying the stream of nitrogen gas on the thin film coaxially and simultaneously with the laser beam comprises spraying nitrogen gas at a pressure of about 600 kPa.

16. The method of making phosphor bronze with surface-embedded titanium carbide particles as recited in claim **12**, wherein the step of scanning the laser beam over the thin film comprises scanning the laser beam at a rate of about 10 cm/s.

* * * * *